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REPORT NO. 7

ANNUAL REPORT
OF
PROGRESS ON INVESTIGATIONS OF CONFECTIONERY FATS

Period Covered: June 1, 1961 - May 31, 1962

Southern Utilization Research and Development Division
Oilseed Crops Laboratory
US New Orleans, Louisiana

United States Department of Agriculture
Agricultural Research Service
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New Orleans, Louisiana

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FOREWORD

This report describes the work of the research team composed of the Fellow of the National Confectioners Association, chemists of the Oilseed Crops Laboratory, engineers of the Engineering and Development Laboratory, and some members of the Spectroscopy Investigations, Cotton Physical Properties Laboratory. Each member of the team is in charge of or responsible for one or more phases of the work.

Dr. Werner Landmann, the Fellow of the National Confectioners Association, assisted in the preparation and evaluation of Cocoa Butter-Like Fat No. 6 (Sections A and B). He carried out a large portion of the work concerned with the new procedure for making a cocoa butter-like fat (Section C), tempering confectionery fats by mechanical working (Section D), the addition of other fats to cocoa butter to improve performance (Section E), and all of the laboratory preparations and characterization of 1-oleodipalmitin (Section F).

The research and development work described in this report is being carried out with the encouragement and support of the National Confectioners

1. The first part of the document discusses the importance of maintaining accurate records of all transactions and activities. It emphasizes the need for transparency and accountability in financial reporting.

2. The second part of the document outlines the various methods and techniques used to collect and analyze data. It includes a detailed description of the experimental procedures and the statistical analysis performed.

3. The third part of the document presents the results of the study. It includes a series of tables and graphs that illustrate the findings of the research. The data shows a clear trend of increasing activity over time.

4. The fourth part of the document discusses the implications of the findings. It suggests that the results have significant implications for the field of study and may lead to further research in this area.

5. The fifth part of the document concludes the study. It summarizes the key findings and provides a final statement on the importance of the research.

Association, its Research Advisory Committee, and the member firms of the Association. Thanks are expressed for their interest, encouragement, and support.

Approved by:

G. E. Goheen, Acting Director

SUMMARY

As requested by the Research Advisory Committee, the preparation of a larger amount of Cocoa Butter-Like Fat No. 5 was undertaken in the pilot plant. This new batch, designated as Fat No. 6, was found to have more desirable properties than did Fat No. 5, an improvement which was attributed to slight differences in the compositions of the starting materials. A portion of the new batch has been distributed for evaluation.

Research was carried out in the laboratory to determine whether the current process for making cocoa butter-like fat could be improved. The procedure investigated was direct esterification of diglycerides with fatty acids in such a manner that random rearrangement, which is generally believed to always accompany this type of reaction, does not occur or is minimized. Preliminary results obtained were very encouraging, and products having good melting characteristics were obtained in high yield.

In the course of laboratory work on the fundamental properties of cocoa butter and other confectionery fats, it was discovered that cocoa butter and other fats, when in the solid state but in unstable crystal forms, could be transformed directly into the stable crystal form by mechanical working. Only a very short period of time is required. The practical importance of this discovery is believed to be very great. It could result in a simplified and more direct process of manufacturing chocolate in that the process could be made truly continuous and the use of tempering kettles could be eliminated.

It was found that mechanical pressure alone will not temper cocoa butter, and also that ultrasonic vibrations have no affect on tempering.

The possibility of increasing the rate of crystal transformation or tempering of cocoa butter by the addition of components of our cocoa butter-like fat also was investigated. These components, which are known to transform at a rapid rate, apparently do increase the rate of transformation of cocoa butter. By means of X-ray diffraction patterns definite proof has been obtained that the tempering of cocoa butter can be hastened by the addition of certain fats closely related to those found in cocoa butter. This information should be of immediate practical value.

1-Oleodipalmitin, another of the components of confectionery fats, has been prepared in pure form, and its characteristics have been determined. This fat possesses two melting points, 65.7 and 95.5° F. Transformation from the low to the high melting form is very rapid. Dilation on melting has been determined.

A relatively simple test devised by other research workers for analyzing cocoa butter for its components was tried and found to work well not only with cocoa butter but also with cocoa butter-like fats and vegetable oils. The technique should be useful for determining the presence of other fats in cocoa butter.

REPORT

A. Preparation of Cocoa Butter-Like Fat

At the last meeting of the Research Advisory Committee of the National Confectioners Association, the decision was made that a larger amount of Cocoa Butter-Like Fat No. 5 should be prepared for further evaluation by confectioners. To prepare this larger amount of fat, completely hydrogenated cottonseed oil and refined olive oil, both commercial products, were obtained from the E. F. Drew Company.

The pilot plant preparation essentially as described in the last annual report was carried out. By way of a brief orientation, the procedure used was as follows: a mixture of 75 pounds of the hydrogenated cottonseed oil and 25 pounds of the olive oil was dried to remove the last trace of moisture. Approximately 0.2% of catalyst was added and the mixture was heated to about 140° F. and stirred for one hour, after which the catalyst was destroyed and removed. The reaction product was dissolved in acetone and cooled to about 68° F. The solid portion that separated from the solution (trisaturated glycerides) was removed and the liquid portion was further cooled to about 33° F. The fraction which crystallized and separated from solution at 33° F. was the crude cocoa butter-like fat. This fraction was given an additional purification treatment by dissolving it in a light hydrocarbon or naphtha boiling between 95 and 140° F. The solution was cooled to 68° F., held at this temperature, and then filtered to remove the small proportion of high melting fat which crystallized out of solution. The filtered solution was stripped to remove the light

hydrocarbon, and the cocoa butter-like fat which remained was given a low-pressure steam distillation to remove any odoriferous components. The finished product will henceforth be designated as Cocoa Butter-Like Fat No. 6. Yields were bigger than those experienced previously.

A few minor changes in the preparation of the cocoa butter-like fat in the pilot plant were made. Previously, the olive oil was purchased in the crude state and then refined, bleached, and deodorized in the laboratory prior to being used. In the **latest** preparations, commercially refined olive oil was used. Formerly, sodium ethoxide which was prepared in our laboratory was used as the rearrangement catalyst; now sodium methoxide, which was purchased and which is used by oil processors in rearrangement reactions, is being used. Tests made in the laboratory indicate some improvements in the pilot plant operation may be possible. The yield of cocoa butter-like fat was increased to over 30% in one laboratory test. The theoretical yield is 42.2%.

The size of the pilot plant is such that 100 pounds of starting materials constitute a convenient batch. Hence, the additional amount of cocoa butter-like fat desired was prepared in four batches.

Fat No. 6 had an iodine value of 29.9, which is slightly below the iodine value of 31.7 for Fat No. 5, and several units below the typical iodine value of cocoa butter, which is about 36.

Melting points determined by the capillary tube method indicated that Fat No. 6 melted over the range of 29 to 35° C. (84 to 95° F.). Dilatometric examinations also were made and from the data obtained the percentage of

liquid component at various temperatures was calculated. The percentages for well-tempered samples of Fat No. 6, Fat No. 5, and cocoa butter are compared in Table I. Fat No. 6 has a melting range which is even more desirable than that for Fat No. 5, and in some respects should be more desirable than that of cocoa butter. It has been found that the domestic olive oil used in the preparation was exceptionally rich in the oleic acid group. Approximately 91% of the component fatty acids was oleic. The percentages of cocoa butter, Fat No. 5, and Fat No. 6 which melted over the temperature interval 86-95° F. were 63.9, 49.6, and 74.0, respectively.

Table I. Liquid Content of Cocoa Butter-Like Fats and Cocoa Butter after Tempering

Temperature °F.	Liquid content, %		
	Cocoa butter	Fat No. 5	Fat No. 6
59	6.8	0.7	-
68	10.8	8.1	6.0
77	16.7	21.7	10.7
86	36.1	46.7	19.3
95	100.0	96.3	93.3
97	-	-	100.0
104	-	96.9	-
113	-	98.5	-
122	-	100.0	-

Fat No. 6, like Fat No. 5, has the desirable property of rapidly solidifying to the stable solid form; that is, practically no tempering is required. A sample aged for one month at room temperature melted over the

same temperature interval as did a sample aged for 16 hours, though the point where most of the melting had occurred was about one degree lower for the latter sample.

A sample of confectionery coating was prepared with Fat No. 6 and a micro-atomized mixture of cocoa powder, sugar, nonfat milk solids, and vanillin and salt. This confectionery coating was hard and had a good gloss. The gloss was unchanged on aging for several weeks at room temperature. The coating on being eaten produced no waxy feel in the mouth. Samples have been sent to several confectioners and interested persons for testing. Comments have not yet been received from all individuals.

B. Additional Experiments with Cocoa
Butter-Like Fat No. 6

Laboratory tests were carried out with the objective of determining whether the process being used to prepare the cocoa butter-like fats could be simplified or improved. Because acetone is more difficult to use in the plant than are light hydrocarbons, fractionation of the reaction product obtained by interesterifying completely hydrogenated cottonseed oil and olive oil was attempted by crystallizing the product from hexane, rather than from acetone. While the cocoa butter-like fats obtained with the two solvents were generally similar, that obtained with hexane as the solvent contained significantly higher proportions of trisaturated and diunsaturated triglycerides;

that is, the fractionation was not as sharp. The probable explanation in terms of physical chemistry is that in the presence of the nonpolar solvent, hexane, hydrogen bonding among the several types of triglycerides became more pronounced and a greater proportion of mixed crystals was produced. The use of hexane as the only solvent had other disadvantages. With hexane, crystallization temperatures lower by about 18 Fahrenheit degrees had to be employed. Also, the second filtration step to remove the crude cocoa butter-like fat was very slow. However, the first filtration to remove the trisaturated glycerides was fairly rapid. On the basis of these tests the conclusion was reached that hexane could not be used as the only solvent for fractionation of the interesterification product.

Laboratory tests also were carried out to determine whether the order of the two fractional crystallizations from acetone could be reversed. Theoretically, the fractional crystallization of a product into three fractions is best accomplished by carrying out first the crystallization at the low temperature to separate the lowest melting fraction as the filtrate and then redissolving the solids and fractionating them at the high temperature. The fractionation of the interesterification product in acetone solution could not be carried out satisfactorily in this manner when the ratio of acetone to product was 4:1 by weight. For an as yet undetermined reason the filtrate could not be readily removed from the large mass of solids formed in the first step.

In the current process for making cocoa butter-like fat, the semi-purified cocoa butter-like fraction is dissolved in an equal weight of petroleum ether, cooled to 77° F., and a small percentage of high-melting fat which separates out of solution is removed by filtration. Because petroleum ether is used in only this step while acetone is used in the other steps, the overall process could be simplified if acetone could be substituted for the petroleum ether. Tests were made in the laboratory with the following results:

<u>Test No.</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Weight of cocoa butter-like fat, g.	20	20	20	20
Solvent	Acetone	Acetone	Hexane	Pet. ether
Weight of solvent, g.	20	40	20	20
Precipitate, %	1.72	0.75	2.72	2.85
Iodine value of precipitate	5.4	4.7	1.7	2.0

As is evident from these data, the petroleum ether was the best solvent.

A few experiments were carried out relative to finding a technique for solidifying Fat No. 6 in such a manner that it will release easily from a mold. In one experiment the fat was melted until only a few seed crystals remained. The mixture then was poured into a mold which was at room temperature (78° F.), held at room temperature for 5 min., then held at 50° F. for 30 min., and finally returned to room temperature. Very little linear contraction had occurred immediately upon completion of the treatment. However, a fair amount of contraction occurred overnight. Cocoa butter heated to 93° F. and then treated in the manner described exhibited good contraction immediately. The addition of 1% soybean lecithin to Fat No. 6 apparently had no effect on the amount of linear contraction.

C. Discussion of Present Procedure and a New
Procedure for Making Cocoa Butter-Like Fats

Present Procedure. All of the cocoa butter-like fats prepared so far in the laboratory pilot plant have been made by the same procedure; that is, the random rearrangement of olive oil and a completely hydrogenated cottonseed oil, followed by fractional crystallization from acetone to obtain a fraction consisting predominantly of oleodisaturated glycerides of palmitic and stearic acids. The best products prepared are believed to be reasonably good cocoa butter-like fats. They were more compatible with cocoa butter than are the coconut oil-containing hard butters. They were not quite as hard or glossy as is cocoa butter when solidified under the best conditions for cocoa butter. The last made cocoa butter-like fat, Fat No. 6, melted almost completely over a shorter temperature interval than did cocoa butter. The most serious disadvantage of the fats is their tendency to solidify in such a manner so as not to release readily from molds. However, some confectioners have stated that they do not consider this to be a serious disadvantage.

A cost analysis for producing the current cocoa butter-like fats on a plant scale has been made. Based on the process used in the pilot plant, the cost should be about 40 cents per pound. While this is higher than desired, it is still low enough to make the process economically feasible. Indications are that this estimated cost can be lowered by the introduction of certain changes in the method of processing.

On the basis of laboratory tests which have already been made with Fat No. 6, and on the basis of results obtained with Fat No. 5, which was similar, one can reasonably come to the conclusion that a relatively good confectionery fat has been made or can be made by the procedure used up to now. We consider our work in this area to be fairly successful. Just how successful must still be determined with further evaluation and development work with Fat No. 6 and similar fats.

It was realized and stated from the very beginning that the process we have employed up to now in making cocoa butter-like fats should produce good products but these would not be identical with cocoa butter. The development of a relatively inexpensive process for making a fat practically identical with cocoa butter has been the objective at various times of a number of research groups around the world. So far the problem has not been solved. However, in the course of work under another project at the Laboratory we made a discovery which we regard as an important step toward attaining this objective.

The problem of making a very good cocoa butter-like fat has been one of obtaining from other fats the building blocks found in cocoa butter and then arranging these building blocks into the proper structural units and combinations of units. The building blocks found in cocoa butter occur abundantly in domestic fats. The problem has been in isolating these building blocks and in recombining them.

New Procedure. The simplest process of recombination is known chemically as esterification. Heretofore, it was believed generally that esterification always is accompanied by interesterification, a random

rearrangement of the fatty acid groups among the molecules of fat. We discovered that simple esterification can be conducted in the absence of interesterification if the proper catalyst and operating conditions are chosen and the water formed as a by-product of the esterification reaction is removed completely as soon as it is formed.

To obtain further evidence that an esterification could be carried out as stated, an experiment was conducted with highly purified reactants. One of these was 1,3-distearin. It was prepared by first making 1,3-benzylidene glycerol, which was converted successively to 1,3-benzylidene-2-benzylglycerol and 2-benzylglycerol. The latter was acylated with stearoyl chloride to obtain 1,3-distearoyl-2-benzylglycerol. Finally, the benzyl group was removed by hydrogenation to obtain pure 1,3-distearin.

The other reactant, pure oleic acid, was obtained by repeated fractional crystallization of the methyl esters of olive oil fatty acids followed by saponification and acidulation of the pure methyl oleate fraction to recover oleic acid.

When the pure 1,3-distearin was esterified with the pure oleic acid (used in a slight excess), the free fatty acids found in the reaction product contained over 90% oleic. Appropriate analyses of the reaction product also indicated that the glycerides consisted of over 90% oleodistearin.

Lipase hydrolysis of the purified oleodistearin product to remove a portion of the fatty acid groups in the 1- and 3-positions yielded a mixture of 37.4% stearic acid and 62.6% oleic acid. These data indicate that the purified oleodistearin product did not consist solely of 2-oleodistearin.

Cooling curves were obtained for the purified oleodistearin product and for pure 2-oleodistearin and 1-oleodistearin. These curves definitely indicated that the oleodistearin product consisted of a mixture containing a large proportion of 1-oleodistearin.

X-ray diffraction patterns of the purified oleodistearin product were obtained. When these were compared with patterns of known mixtures of 2-oleodistearin and 1-oleodistearin subjected to the same thermal treatment, it appeared that the oleodistearin product consisted of about 75% 1-oleodistearin and 25% 2-oleodistearin.

These data confirm that diglycerides can be esterified without interesterification occurring, though some isomerization of the diglycerides occurs prior to esterification. A consideration of the probable kinetics involved indicates that the effect of isomerization possibly can be circumvented. It should be possible to make good cocoa butter-like fats by the simple esterification of diglycerides which can be manufactured readily on a large scale.

By way of preliminary experiments, five cocoa butter-like fat products were prepared by esterifying oleic acid with the diglycerides of palmitic and stearic acids. The diglycerides were obtained from a potential manufacturer of these compounds as molecularly distilled diglycerides of completely hydrogenated lard. It is not known at this time if the diglycerides contained a small amount of saturated triglycerides. The oleic acid was derived from olive oil.

In each esterification run the diglycerides and oleic acid were dissolved in dry mineral spirits (about 4 parts of mineral spirits to 1 of reactants) and the solution was added slowly to boiling mineral spirits.

The catalyst, when one was employed was added in 2 to 4 portions during the course of the reaction. The water produced during the course of the esterification was removed continuously by the boiling mineral spirits. The reactants were added in the course of 3 hr., and then the reaction was continued for an additional hour. At the end of the 4 hr. all mineral spirits were removed from the reaction product by bubbling nitrogen, an inert gas, through the mixture.

The uncombined oleic acid was removed from the crude reaction product by an alkali refining procedure customarily employed with fats and oils. The refined fat was dissolved in an equal weight of light hydrocarbon and cooled to room temperature to crystallize the saturated di- and triglycerides, which were removed by filtration. The cocoa butter-like fat then was recovered from the liquid portion. The yield of cocoa butter-like fat, calculated on a total glyceride basis, was as high as 83%. The yield and iodine value of the cocoa butter-like fat obtained in each run was as follows:

<u>Fat</u>	<u>Iodine value</u>	<u>Yield</u>
EP-1	32.7	76%
EP-2	34.0	83%
EP-3	34.6	70%
EP-4	35.2	50%
EP-5	28.0	46%

Fats EP-1 and EP-2 were made with the aid of the preferred catalyst, p-toluenesulfonic acid. So far this catalyst has been found to produce the highest yield, but the color of the product is about that of cocoa butter. In the preparation of Fats EP-3 and EP-4, stannous chloride was used as

catalyst. The latter gives lower yields, but the end product is almost water white. Fat EP-5 was produced without the aid of a catalyst. The yield here is considered to be unacceptable.

Cocoa Butter-Like Fats No. EP-1, -2, -3, and -4 were examined dilatometrically. The liquid contents of well-tempered samples were calculated and are compared in Table II with those of cocoa butter and Cocoa Butter-Like Fat No. 6.

Table II. Liquid Content of Cocoa Butter-Like Fats and Cocoa Butter After Tempering

Temperature °F.	Liquid content, %					
	Cocoa butter	Fat No. 6	Fat EP-1	Fat EP-2	Fat EP-3	Fat EP-4
50	--	--	--	0.6	1.2	2.0
59	6.8	--	0.6	4.0	7.1	9.1
68	10.8	6.0	3.6	14.7	15.7	19.5
77	16.7	10.7	3.8	24.8	22.4	27.7
86	36.1	19.3	19.5	40.6	40.6	47.8
95	100.0	93.3	67.0	79.0	76.8	76.0
97	--	100.0	--	--	--	--
104	--	--	92.0	96.0	94.4	92.4
109	--	--	--	100.0	--	--
111	--	--	100.0	--	100.0	100.0

It can be concluded that the newly discovered esterification procedure should be a good one for making cocoa butter-like fats. In its present form it should be suitable for use on a plant scale. However, we believe that the procedure can be further improved and simplified. Work toward accomplishing this is underway. Different reaction conditions and different starting materials are now being tried.

D. Tempering Confectionery Fats by Mechanical Working

The tempering of chocolate and other fat-containing confections is one of the troublesome operations carried out by the confectioner. Ordinarily one or more tempering kettles are employed to condition the semi-melted chocolate prior to the molding or enrobing operation. Insufficient tempering may result in fat bloom. Overtempering results in a coarse texture and bad appearance. The problem is to introduce just the right type, amount, and size of seed crystals. Each of the major components of cocoa butter ordinarily can solidify in four crystal forms. The one desired in tempered chocolate is the highest melting or stable form.

Several aspects of the problem of tempering have been discussed at various times with different individuals of the Research Advisory Committee. A suggested approach to insuring proper temper was the finding of a material, preferably edible and digestible, or at least non-toxic, which would have a melting point above that of cocoa butter and would serve, when properly dispersed, as nuclei for the highest-melting crystal form of the components of cocoa butter. In other words, cocoa butter would be seeded in a manner analogous to the seeding of clouds with silver iodide to produce ice crystals. Some progress has been made in this direction, and the approach will be explored further. In the meantime, we discovered in our laboratory that the lower melting or unstable crystal forms of cocoa butter and other fats can be converted to the stable form by intense mechanical working.

The mechanical working which is required to bring about the conversion of the unstable crystals of fat to stable crystals is much greater than that encountered in the enrober or tempering kettle. The single, individual crystals actually must be deformed and kneaded. In laboratory experiments this mechanical working was accomplished by forcing almost completely solidified fat repeatedly through small orifices at pressures up to 1000 pounds per square inch. Two of the experiments which were carried out are described below.

Commercial cocoa butter was melted and heated to about 160° F. to destroy all crystal nuclei. A thin layer of the melt was poured into a beaker and solidified rapidly. The beaker was taken into a walk-in cooler, kept at 40° F., and a portion of the cocoa butter was removed and extruded repeatedly through a small orifice at high pressure. Sufficient time was allowed between extrusions so that the temperature of the extruded cocoa butter always remained below about 50° F., and no visible melting occurred. After a few extrusions the butter became much harder. A total of ten extrusions was made. Then the worked and unworked cocoa butter were forced into separate molds and X-ray diffraction patterns obtained. The mechanically worked portion of the cocoa butter exhibited the characteristic lines of a well-tempered and aged sample; that is, the components of the worked sample of butter were in the highest-melting, stable crystal form. These characteristic lines were absent in the X-ray diffraction pattern of the quickly solidified but unworked portion of the sample. These data are positive proof that cocoa butter solidified in unstable crystal forms is converted to the stable form by mechanical working.

In the other experiment chocolate liquor was melted and heated to 153° F., to destroy all of the crystals of cocoa fat. The chocolate liquor then was quickly solidified by cooling the beaker containing it in an ice bath. The beaker and its contents were taken into the walk-in cooler, kept at 40° F., and a portion of the solidified chocolate liquor was removed from the beaker and extruded ten times through a small orifice.

When the worked and unworked portions were warmed to room temperature, 77° F., partial melting of the unworked portion occurred; but the worked portion did not melt. Both portions were heated to 93° F., at which temperature most of the solid fat melted. Both portions were kept at this temperature for one-half hour, then poured into molds and solidified by storing in a refrigerator for one-half hour at 41° F. The temperature of the samples then was allowed to increase gradually and hardness tests were made as the temperature increased. The molded pieces made from the worked sample always were two to three times harder than those made from the unworked sample. It was determined in earlier work that the hardness of a sample of chocolate increases as the fat crystals transform to the highest melting polymorphic form. The conclusion can be drawn that working the solid cocoa fat converted some or all to the stable crystal form, and the seed crystals which remained after partial remelting and molding were sufficient to cause the molded chocolate liquor to solidify or convert rapidly to the stable form.

Examination of the molded bars at room temperature revealed that those made from the worked chocolate liquor possessed a good gloss and good

contraction and could be demolded readily; whereas those made with the unworked chocolate liquor possessed poor gloss and poor contraction and could not be demolded. The bars made from the worked chocolate liquor behaved in every respect like bars made from chocolate liquor which had been seeded adequately with crystals of the stable polymorphic form of cocoa butter.

The discovery that a solid to solid transformation of fat crystals can be effected by mechanical working is considered to be highly important and to have important practical applications. It is believed that through the use of this discovery improvements in the manufacture of chocolate and chocolate-type confections can be accomplished. Probably the use of tempering kettles can be eliminated, the enrobing machines can be simplified, and a truly continuous process can be devised in which the material in actual process is perfectly tempered and always small in amount. In such a modified process crushed or granulated chocolate would be fed continuously into a heat exchanger where the chocolate would first be melted and then cooled until some unstable fat crystals formed. This mixture would then be forced through a series of orifices and pumped to the enrober or molding machine. Possibly only a portion of the flow to the latter machines might be forced through the orifices.

An article giving additional data and details on the mechanical working of solid fats has been prepared for publication. It is entitled "Tempering Triglycerides by Mechanical Working," and was presented at the fall meeting of the American Oil Chemists' Society and has now been

submitted for publication in the Journal of the Society. The discovery has also been discussed with a number of individuals and helpful suggestions have been received with regard to further development. According to one suggestion, simple pressure might be sufficient to bring about the tempering. This was tried. A sample of cocoa butter was heated far above its melting point and then quickly solidified. A portion of the sample was put into a press; and while the press and surrounding atmosphere were kept at 40° F., a mechanical pressure of 7,600 lb. per sq. in. was applied for a period of 2 hr. This treatment did not produce any tempering.

According to another suggestion, ultrasonic vibrations might be able to temper a fat. To test this possibility, two ultrasonic machines were used. One operated at a frequency of 40 kilocycles and a power of 500 watts and was equipped with a tank having an area of about 0.5 sq. ft. The other operated at 90 kilocycles and a power of 40 watts and was equipped with a tank having an area of about 0.25 sq. ft. Small samples of quickly solidified cocoa butter were immersed in water in the tanks. The water and the samples were maintained at 40° F. Treatment time was about 15 minutes. The ultrasonic vibrations did not temper the cocoa butter.

E. Improvement in the Performance of Cocoa Butter
by the Addition of Other Fats

In the last annual report reference was made to data indicating that the addition of some individual components of Cocoa Butter-Like Fat No. 5 to individual components of cocoa butter greatly increased the rates of polymorphic transformation of the latter. The individual components of

Cocoa Butter-Like Fat No. 5 which were investigated transformed to the highest-melting crystal form at a very rapid rate. These conclusions were further supported by dilatometric data on confectionery coatings made with Fat No. 5 and with cocoa butter. The coatings made with Fat No. 5 could be tempered quite readily so that the fatty components were in the highest melting form, even though 30% of these fat components were identical with those of cocoa butter.

On the basis of these data it was thought that the addition of Fat No. 5 to cocoa butter might be a practical means of speeding the transformation of all the fat crystals in the mixture to the highest melting polymorphic form. Therefore, a series of experiments was undertaken in which the dilatometric properties of various mixtures of 1-oleodistearin, an important component of Fat No. 5, and 2-oleodistearin, a main component of cocoa butter, were investigated. Also, mixtures of Fat No. 5 and 2-oleodistearin were investigated. Special, volumetric-type dilatometers using only about one gram of fat each were employed in order that the melting curves could be determined rapidly. For comparison, dilatometric curves of 2-oleodistearin and of Fat No. 5 were determined under the same operating conditions. The dilatometric determinations were made on quickly solidified mixtures after tempering for 1, 16, and 240 hours.

The data obtained show that the rate of transformation of the fast-transforming component is definitely slowed by the addition of another component or fat mixture. However, when the added component has a slow rate of transformation when alone, its rate of transformation definitely

appears to be increased on being mixed. The exact behavior depends upon the composition of the mixture. In some mixtures the two components behave as a single compound, at least on the basis of dilatometric data, while in other mixtures they tend to behave as individual components and each to some extent appears to melt independently of the other. The behavior of the mixture undoubtedly is complicated by the formation of solid solutions and eutectics.

X-ray diffraction patterns of various quickly solidified mixtures of 1-oleodistearin and 2-oleodistearin were obtained after aging at 77° F. for 1, 16, and 240 hours. In most of these mixtures the individual components exhibited their characteristic diffraction lines, indicating not only the presence of the component but also its crystal form. Definite proof was obtained that the addition of 1-oleodistearin to 2-oleodistearin increased the rate of polymorphic transformation of the latter to the stable form. The practical value of this information is, of course, obvious---the cocoa butter in chocolate is more easily tempered if certain types of fat are added.

One of the mixtures which was examined, that containing 25% 2-oleodistearin and 75% 1-oleodistearin, behaved in a peculiar manner. X-ray diffraction lines appeared which indicated the presence of a new-type crystal, probably a mixed crystal. In the earlier dilatometric examination this mixture also behaved in a peculiar manner. The dilatometric curve resembled that of a single, pure compound.

F. Preparation and Characterization of 1-Oleodipalmitin

1-Oleodipalmitin, another of the components occurring in confectionery fats, was prepared in a pure state. The following method of synthesis was employed: 1-Monoolein (1 mole) was dissolved in dry chloroform containing dry quinoline (3 moles). Palmitoyl chloride (2.1 moles) was added slowly, with shaking. The mixture was placed in an incubator at 45° C. (113° F.) for three days. The mixture then was dissolved in diethyl ether and washed successively with 0.5 N sulfuric acid, 5% potassium bicarbonate solution, and water. The semi-purified product was crystallized several times from acetone solution.

The capillary melting point of the compound after crystallization from acetone was 35.3° C. (95.5° F.). The melting point of a quickly solidified sample was 18.7° C. (65.7° F.). The iodine value was 30.2 (theoretical, 30.5).

1-Oleodipalmitin was found to be similar to 1-oleodistearin in that only two melting points were found, and the low-melting form converted very rapidly at or near its melting point to the high-melting form. Melting dilation of the high-melting form was 0.1121 ml./g., measured at the dilatometric melting point of 33.3° C. (91.9° F.). The melting dilation of the low-melting form was 0.0618 ml./g., measured at 18.7° C. (65.7° F.).

G. Analytical Procedure for Separating Confectionery Fats into Their Major Components

In the course of examining the various cocoa butter-like fats and cocoa butter a simple paper chromatographic test devised by Steiner and Bonar (J. Sci. Food Agric., Vol. 12, pp. 247-250 (1961)) was tried. The test was found to be quite good. Cocoa butter could readily be separated

into three major components: oleodistearin, oleopalmitostearin, and oleodipalmitin. Three separate spots were obtained on the test paper. The positions of the spots for cocoa butter differed from those for the cocoa butter-like fats, and those for vegetable oils. The procedure could prove to be quite useful in detecting the addition of other fats to cocoa butter.

Briefly, the procedure consists of putting a small sample of the fat on an 18-inch strip of filter paper which has been treated with liquid paraffin. The paper is mounted in a glass jar and the spot of fat fractionated by allowing a solution of acetone-methanol (90:10) saturated with paraffin to descend along the strip. Iodine vapors are employed to locate the fat fractions.

The distance traveled (degree of separation) by the individual triglycerides is dependent on the chain length of the component fatty acids and on the degree of unsaturation of the triglycerides. The shorter the chain length of the fatty acid groups and the more unsaturation in the fat molecule the further the spot will be from the origin. We have separated cottonseed and olive oils into several components by this procedure.

